

The University of Chicago

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RELATIONS OF MONOMOLECULAR FILMS. II.
d-PIMARIC ACID AND TETRAHYDRO-*d*-
PIMARIC ACID**

**II. THE REARRANGEMENT OF MOLECULES
IN PLASTIC MONOMOLECULAR FILMS: PRES-
SURE-AREA AND POTENTIAL RELATIONS FOR
POLYCYCLIC COMPOUNDS OF THE FIVE-RING
SERIES**

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1936

By
EVERETT F. CARMAN

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CHICAGO, ILLINOIS

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Surface Potentials and Force-Area Relations of Monomolecular Films. II. *d*-Pimaric Acid and Tetrahydro-*d*-pimaric Acid

I. Introduction

Through the kindness of Professor Ruzicka the writer has been able to investigate the surface potentials and force-area relations of *d*-pimaric acid, an unsaturated compound, and tetrahydro-*d*-pimaric acid, the corresponding saturated compound. These compounds contain a phenanthrene residue, and are related to certain hormones and vitamins. The carboxyl group is displaced one position from the hydroxyl group of cholesterol, and the area for the pimaric acid is slightly larger.

II. Apparatus and Procedure

The apparatus and general procedure are essentially the same as described by Harkins and Fischer.¹ The modifications that have been introduced will appear in a paper which is now being prepared for publication. A more recent improvement will be discussed here in connection with the method adopted to obtain "zero" or clean surface potentials. It has increased the accuracy of the surface potential values.

The procedure is as follows. The trough is filled with the aqueous solution (0.01 molal hydrochloric acid in these experiments) and the surface swept several times to remove initial contamination. The electrode is then lowered into a position 2 to 3 mm. above the surface and the cage closed. The system is allowed to remain in this condition for about one hour. It seems that during this time most of the additional contamination settles out from above the surface and rises from below. At the same time the surface of the silver-polonium electrode reaches equilibrium with the water vapor.

One of the features of the procedure involves the use of mechanical arms to perform the final sweepings without opening the cage or otherwise disturbing the immediate surroundings of either the surface or the electrode. It is unnecessary to raise the electrode in order to accomplish the final sweepings as thin barriers have been constructed which easily pass under the lowered silver-polonium disk. After the hour has elapsed, the surface is swept until the potential is constant to within 1 mv. for periods of ten to twenty minutes. Readings are taken immediately after the individual sweepings to ensure a clean surface during the measurement. The additional barriers for the final sweepings are taken from racks conveniently suspended above the two ends of the tray.

The importance of an accurate clean surface potential

cannot be overemphasized, as it is obvious that an error here vitiates all of the film potential values. It might be added in connection with these precautions that capillary active contamination falling on the spread films has a negligible effect on the potential compared to the change introduced by the same contamination on a cleaned surface.

The films were spread from redistilled benzene solutions on 0.01 molal aqueous hydrochloric acid. Surface potential and pressure measurements were made simultaneously at minute intervals. The experiments were carried out at room temperature (28 to 30°).

III. Pressure-Area Relations and Thickness of the Films

The saturated and unsaturated compounds form monomolecular films, which give almost identical pressure-area curves until collapse begins (Figs. 1, 2 and 3). The film which is composed of the unsaturated compound withstands higher pressures than that of the saturated, and its maximum pressure is about 17 dynes on 0.01 molal hydrogen chloride. The film pressure of the unsaturated compound approaches a state of equilibrium. The maximum thickness of the mono-layer is about 12 Å. for both compounds, or slightly less than half that for a similar film of stearic acid. These compounds exhibit orientation of the perpendicular type. The films are much thicker than those in which a single chain lies flat in the surface.

The films are highly compressible, and the coefficient $[(a_0 - a_1)/a_0]/(f_1 - f_0)$ has a value of 0.0068 for the saturated acid and 0.010 for the unsaturated compound.

The extrapolated molecular area at zero pressure for both the saturated and unsaturated compounds is about 53 sq. Å. but it seems possible to compress the films to an area of about 43 sq. Å. before collapse occurs. This is practically the area of two hydrocarbon chains. Our unpublished data on large rings up to thirty-four carbon atoms in the ring, and the values of Büchner, Katz and Samwel² on rings up to thirty carbon atoms, also give minimum areas equal to that exhibited by two single oriented hydrocarbon chains.

(1) Harkins and Fischer, *J. Chem. Phys.*, **1**, 852 (1933).

(2) Büchner, Katz and Samwel, *Z. physik. Chem.*, **B5**, 327 (1929).

The work of Harkins and Morgan³ showed that phenanthrene spreads on water only when much salt is present. The compounds used in our work are much more saturated, which probably reduces resonance in the molecule, but has only a minor effect on the polarity. However, the presence of the dipole due to the carboxyl group, as is usual, orients the molecule with this group toward the water.

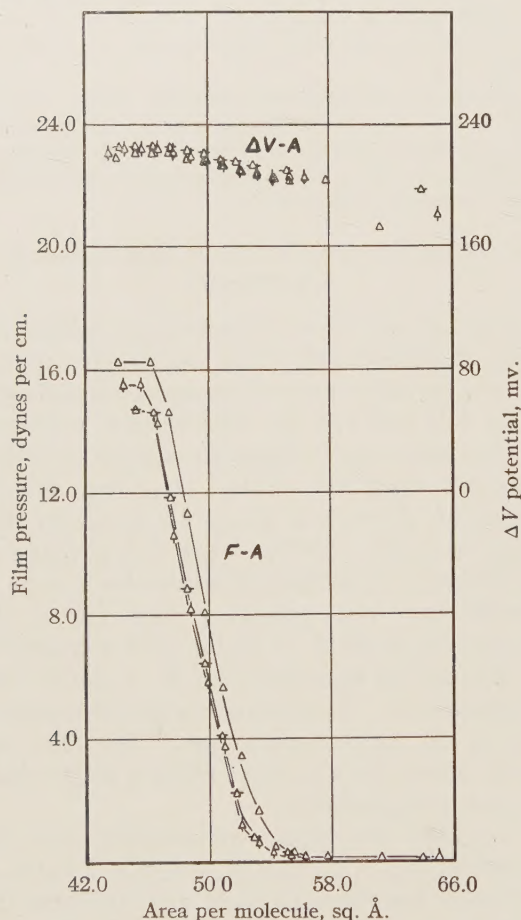


Fig. 1.—Tetrahydro-*d*-pimaric acid on 0.01 molal hydrochloric acid.

	Expt.	Temp. °C
Δ	199	28.0
△	200	28.0
-Δ-	206	29.5

IV. Structure and Orientation of the Pimaric Acids

It is of interest to compare the structures and orientations in films of the pimaric acids with those of cholesterol. If the side chains, which, due to interpenetration of the molecules probably contribute very slightly to the cross-sectional

area, are neglected the similarity between the pimaric acid nucleus (phenanthrene residue) and the A, B, C ring structure of cholesterol (Fig. 4) is obvious. The significant point of difference is the location of the polar, water-attracting group.

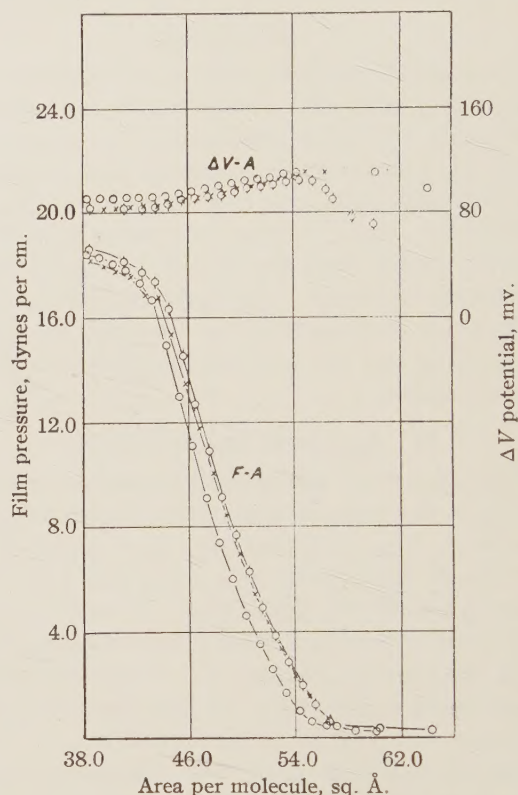


Fig. 2.—*d*-Pimaric acid on 0.01 molal hydrochloric acid.

	Expt.	Temp. °C.
×	197	30.0
○	198	28.0
○	205	28.0

In pimaric acid the carboxyl group is on carbon atom number 4, whereas in the cholesterol compound the hydroxyl group occupies position number 3. It is evident that if the molecule is oriented so that the polar group is located at the lowest point, one would expect the pimaric acids should be tilted in such a way as to occupy more area in the surface than the vertically oriented cholesterol. The cross-sectional area of a molecule obtained from film balance measurements is of course dependent on the orientation.

Measurements of molecular models indicate that for oriented sterol ring systems with the polar group in position 3, the cross-sectional area should be about 37 sq. Å. and for the same system with the polar group in position 4 about 42

(3) Harkins and Morgan, *Proc. Nat. Acad. Sci.*, **11**, 637 (1925).

sq. Å. Measurements on models and the effects of the positions of polar groups in similar compounds have been discussed in a paper by Danielli and Adam.⁴ The calculations agree quite well with the film areas per molecule at the collapse pressure. The area obtained for the unsaturated acid at the collapse pressure is about 43 sq. Å. The extrapolated area, 53 sq. Å., is considerably greater because of the expanded nature of the film.

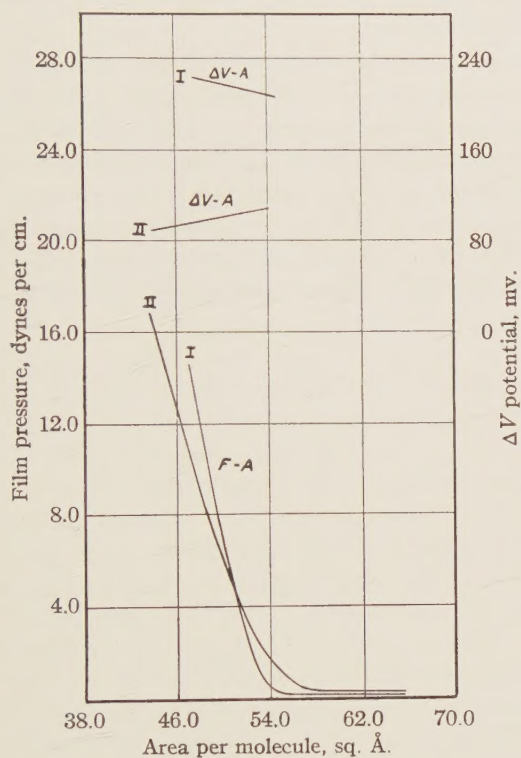


Fig. 3.—Average curves: I, tetrahydro-*d*-pimarinic acid; II, *d*-pimarinic acid.

It may be noted here that the curve of the more condensed film of tetrahydro-*d*-pimarinic acid crosses the curve for the unsaturated acid. Consequently, the reduced compound has a larger area at the collapse point and a smaller extrapolated area at zero pressure than does the unsaturated acid. The increased polarity of the unsaturated compound is probably the cause of the expanded nature of the film. This will also account for the greater adhesion to the water surface and the resultant higher pressure.

V. Surface Potentials

The surface potential (ΔV), defined as the difference in the contact potential when the film

is present and when it is absent, exhibits some anomalies not previously found. The surface potentials of the condensed films are low, with a value of about 100 mv. for the unsaturated and about 200 mv. for the saturated compound. The film of *d*-pimarinic acid exhibits a behavior heretofore unobserved in that the surface potential of the condensed film *decreases* as the film is compressed.

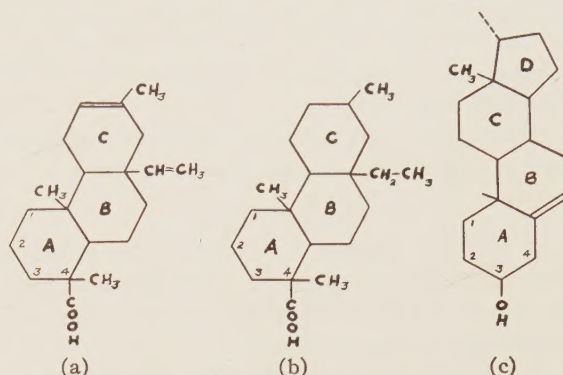


Fig. 4.—Vertical orientation of molecules at air-water interface: (a) *d*-pimarinic acid; (b) tetrahydro-*d*-pimarinic acid; (c) cholesterol (chain omitted).

In connection with the surface potential of tetrahydro-*d*-pimarinic acid, it should be noted that the measurements for this compound gave about 200 mv., which is approximately half of the value obtained for a straight chain acid of the type of stearic acid. This is largely because the area per molecule or area per polar group for this reduced pimarinic acid is roughly twice that of the stearic acid type, so its polar group surface density is approximately half that of condensed stearic acid films. However, there are a number of complicating factors which include effects due to orientation of adjacent dipoles, water dipoles, and shifts of electrolyte ions.

As indicated above the surface potential of the unsaturated *d*-pimarinic acid is about 100 mv., or one-half that of the saturated compound, although the two substances have practically the same molecular surface density. One would therefore be led to believe that the dipoles associated with the double bond in the ring or in the side chain or possibly in both are oriented in such a way as to oppose the dipole of the carboxyl group, even at the initial stages of the compression. Then, on compression, further internal opposition or compensation of the dipoles may be said to result in the decreasing surface potential observed. As shown by Harkins, Ries and Carman⁵ the surface

(4) Danielli and Adam, *Biochem. J.*, **28**, 1583 (1934).

(5) Harkins, Ries and Carman, *THIS JOURNAL*, **57**, 776 (1935).

potential (ΔV) may rise considerably less rapidly than the surface density of the film (13% less rapidly in the case of certain polymers of ω -hydroxydecanoic acid). This is usually attributed to the mutual effect of the surrounding dipoles. However, it is quite probable that in the case of the *d*-pimaric acid, the conspicuous *decrease* in the surface potential with increased surface density is due to a changing orientation of the individual molecules in such manner as to further the opposition or compensation of the intramolecular dipoles.

Additional studies relating potential variations to temperature changes are now in progress.

VI. Summary

1. Surface potential and force-area relations for monomolecular films of a saturated and unsaturated pimaric acid were studied. The corresponding curves are shown.

2. An improved procedure for obtaining more

accurate clean-surface potentials is described.

3. The maximum thickness of the mono-layer is about 12 Å. for both compounds. The coefficients of compressibility are calculated.

4. The structures of the pimaric acids are compared with that of cholesterol, and their orientations in surface films are related to the different positions in which the polar groups are located. The experimental data compare favorably with the results to be expected from model measurements.

5. The surface potential of the tetrahydro-*d*-pimaric acid is about 200 mv., whereas that of the unsaturated compound is about 100 mv. An unprecedented decrease in the surface potential on compression was observed in the case of the unsaturated acid films. It is considered probable that these facts may be related to an increasing intramolecular dipole compensation on compression.

The Rearrangement of Molecules in Plastic Monomolecular Films: Pressure-Area and Potential Relations for Polycyclic Compounds of the Five-Ring Series

1. Introduction

Monomolecular films of certain compounds whose molecules contain five benzene rings have been found to exhibit a remarkable phenomenon. That is, a rapid rearrangement of the molecules occurs in the film in such a way that the pressure at the initial area almost disappears. Thus with betuline the initial or immediate pressure at a molecular area of 34.5 sq. Å. is 17 dynes per cm. while after this there is at this area an almost exponential fall of pressure with time to a practically constant value of 1.0 dyne. Nevertheless, a rapid compression to 33.5 sq. Å., or by about $1/34$ of the area, increases the pressure by 21 times to 21 dynes, or to 4 dynes more than the previous initial compression. At an area of 28 sq. Å. the initial pressure of 40 dynes falls to 5.5 dynes in thirty seconds, but on rapid compression to 26.2 sq. Å. rises to 50 dynes per cm.

The set of six polycyclic compounds was made available through the kindness of Professor Ruzicka. The molecules of these compounds contain a phenanthrene residue (Figs. 1 and 2) as did the *d*-pimaric acids (Fig. 3) investigated in this Laboratory by Harkins, Ries and Carman.¹ A comparison of the surface potentials and force-area relations of the monomolecular films formed by this series (Figs. 4, 5, 6) is of considerable value, since the compounds (supposedly) differ only in their polar substituents.

The writers had the privilege of discussing the proposed structures with Professor Ruzicka (August, 1935), who tentatively assigned the polar groups to the locations suggested in Fig. 1. These proposed structures have not been definitely established, as yet, particularly with reference to the location of some of the polar groups. This fact must be borne in mind throughout the following discussion, as to cite all the possibilities at each reference to structure is not practicable.

2. Apparatus and Procedure

The apparatus is essentially the same as that described by Harkins and Fischer² and modified

by Harkins, Carman and Ries.³ The improved method of determining "zero" or clean surface potentials as described by Harkins, Ries and Carman¹ has been used throughout these experiments.

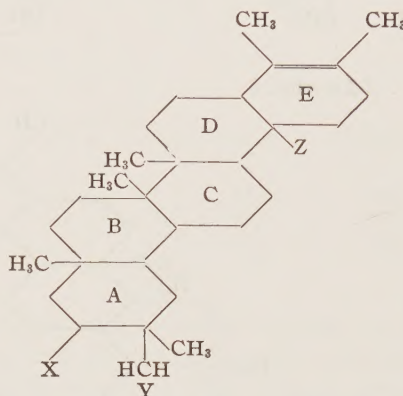


Fig. 1.—General structure of the five-ring compounds.

A modification in the older technique was made to obtain certain effects important in this investigation. As the area of the film was decreased, the torsion wire was turned simultaneously with the movement of the compression barrier. The pressure thus remained balanced during compression and instantaneous pressure readings were obtained. The compression barrier was moved at intervals of one minute and pressure readings taken immediately (unbroken lines) and then thirty seconds later (dotted lines; Figs. 4-6).

The compounds were dissolved in twice distilled chloroform and the films spread on 0.01 molal aqueous hydrochloric acid. The experiments were conducted at room temperature (24-29°) in a metal box covered with a thermal insulation.

3. Pressure-Area Relations

The pressure-area relations for these compounds are shown in Figs. 3-9 and Table I. The condensed films of these substances are of the solid type similar to those of stearic acid. This was demonstrated by the immobility of particles of lycopodium powder on their surface under a jet of air.

(1) Harkins, Ries and Carman, *J. Am. Chem. Soc.*, **57**, 2224 (1935).

(2) Harkins and Fischer, *J. Chem. Phys.*, **1**, 852 (1933).

(3) Harkins, Carman and Ries, *ibid.*, **3**, 692 (1935).

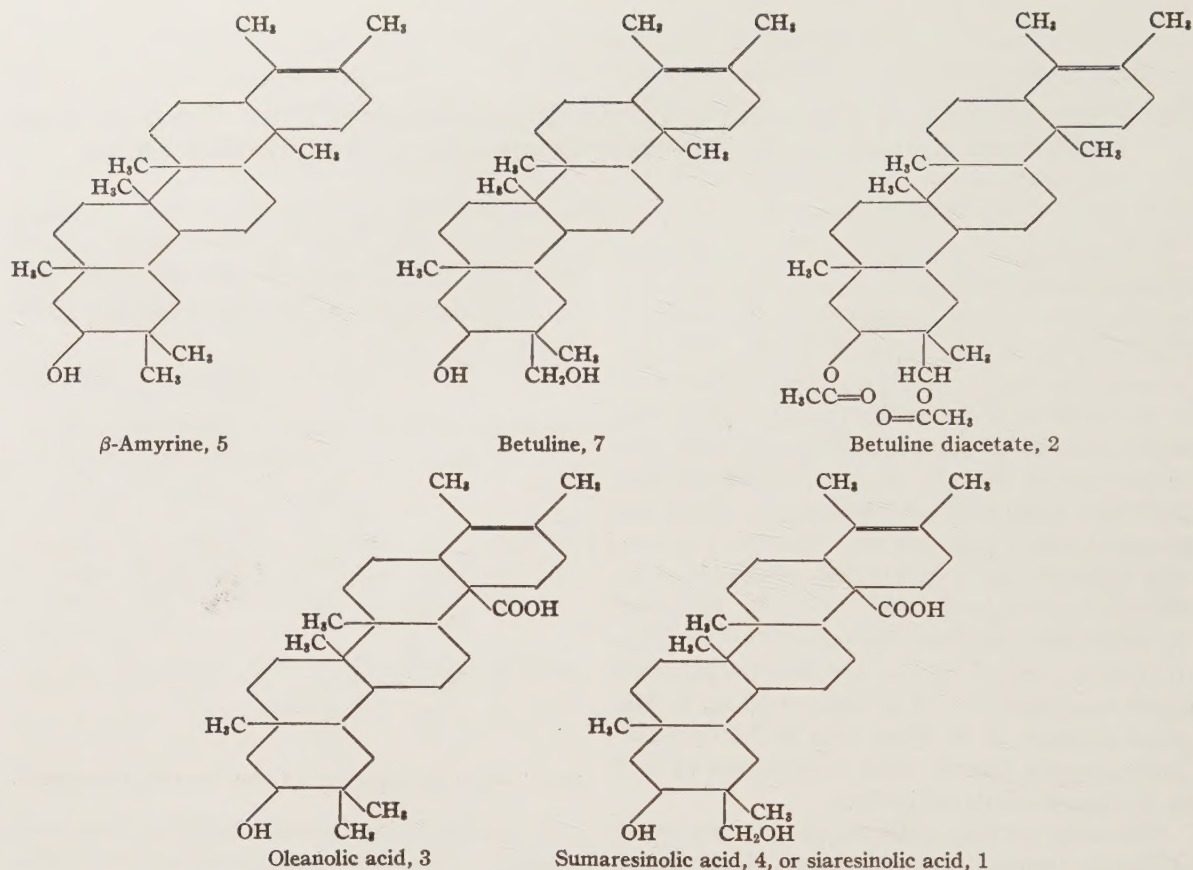


Fig. 2.—Structure of the five-ring compounds (the numbers refer to numbers on the figures).

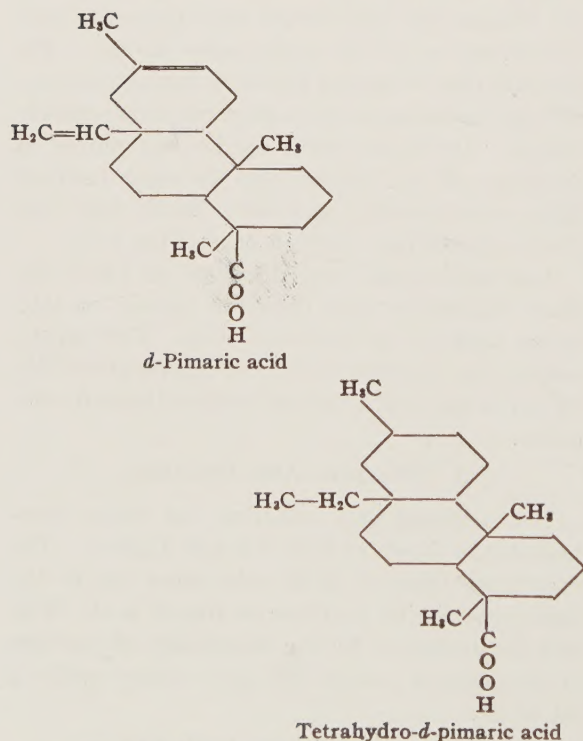


Fig. 3.—Structure of the pimaric acids.

The compressibility coefficients $\frac{(a_0 - a_1/a_0)}{f_1 - f_0}$, given in Table I are calculated from the slopes of the curves at pressures just below those of collapse. These coefficients range from 0.0033 to 0.0103 (stearic acid = 0.00763), and are normal for solid condensed films with perpendicular orientation of the molecules. The compressibility coefficient for tetrahydro *d*-pimaric acid, which has a three-ring structure, is greater than for any of the five-ring compounds, except betuline diacetate. This was to be expected, as pointed out by Harkins, Carman and Ries,³ since the compressibility of films of vertically oriented molecules decreases with increasing length while that of horizontally oriented molecules is independent of the length. In betuline diacetate the high compressibility is related to the presence of the ester groups.

It may be noted here that at the lower portion of the curves, especially in the case of oleanolic, sumaresinolic and siarsesinolic acids, each of which is supposed to contain a carboxyl group at Z in the upper part of the molecule (Fig. 1), the compressibility coefficients are very much larger.

TABLE I

PRESSURE-AREA RELATIONS OF MONOMOLECULAR FILMS OF POLYCYCLIC COMPOUNDS OF THE FIVE-RING SERIES
INITIAL NON-CONTRACTED FILMS

Compounds	Mol. wt.	Density	Vol. of molecule, cu. Å.	Area per molecule at a film pressure			Max. press. f_m	t = Film thickness of film at a film pressure			Compressibility at $f=0$
				$f=0$	$f=10$	$f=\text{max.}$		$f=0$	$f=10$	$f=\text{max.}$	
β -Amyrine	426.4	0.92	765	46.8	45.2	43.4	22.0	16.3	16.9	17.6	0.0033
Betuline	442.4	.92	792	37.2	37.4	26.4	49.8	21.3	21.2	(30.0)	.0059
Betuline diacetate	526.4	1.0	868	52.6	Collapse	47.6	9.2	16.5	Collapse	18.2	.0103
Oleanolic acid	456.4	0.94	801	55.4	56.6	43.0	47.8	14.5	14.1	18.6	.0047
Sumaresinolic acid	472.4	.92	846	51.0	51.0	43.0	44.8	16.6	16.6	19.7	.0035
Siaresinolic acid	472.4	.94	828	49.0	49.4	37.5	48.0	16.9	16.8	22.8	.0049
Tetrahydro- <i>d</i> -pimaric acid	306.3	1.0	506	52.3	48.8	47.1	14.7	9.70	10.4	10.7	.0068

CONTRACTED FILMS

Contracted curve		CONTRACTED FILMS						
β -Amyrine	See initial values							
Betuline	24.1	26.2	22.0	44.0	32.8	30.2	36.0	0.00198
Betuline diacetate	See initial values							
Oleanolic acid	47.2	47.0	43.0	29.6	17.0	17.1	18.6	.0030
Sumaresinolic acid	51.8	47.8	39.8	24.0	16.3	17.7	21.2	.00965
Siaresinolic acid	42.2	42.6	35.8	33.6	19.6	19.4	23.1	.0045
Tetrahydro- <i>d</i> -pimaric acid	See initial values							

It is interesting to compare the extrapolated areas per molecule at the collapse pressure. The areas for β -amyrine, oleanolic acid and sumaresinolic acid are approximately 43 sq. Å. Betuline gives a much smaller area of about 26 sq. Å. while tetrahydro-*d*-pimaric acid and betuline diacetate give larger areas of about 47 and 48 sq. Å., respectively.

There seems to be some relation between collapse pressure and the number and kind of polar groups in the molecule. Tetrahydro-*d*-pimaric acid with three rings and one carboxyl group has a collapse pressure of about 15.0 dynes per cm.; β -amyrine, which contains one hydroxyl group at X and a double bond in ring E has a higher collapse pressure of about 22 dynes per cm. Betuline, oleanolic acid and siaresinolic acid have collapse pressures of about 48 dynes per cm. while that of sumaresinolic acid is about 45 dynes per cm. All of these compounds which exhibit collapse pressures only slightly below 50 dynes, have either two or three polar groups beside the double bond in ring E (Fig. 1). The fact that the adhesion of the film for the substratum is greatly increased in these latter compounds is undoubtedly related to the addition of polar groups to the molecule. By com-

paring betuline with betuline diacetate the effect of changing from two hydroxyl to two acetyl groups is very clearly shown in their collapse pressures. Betuline has a collapse pressure of about 48 dynes

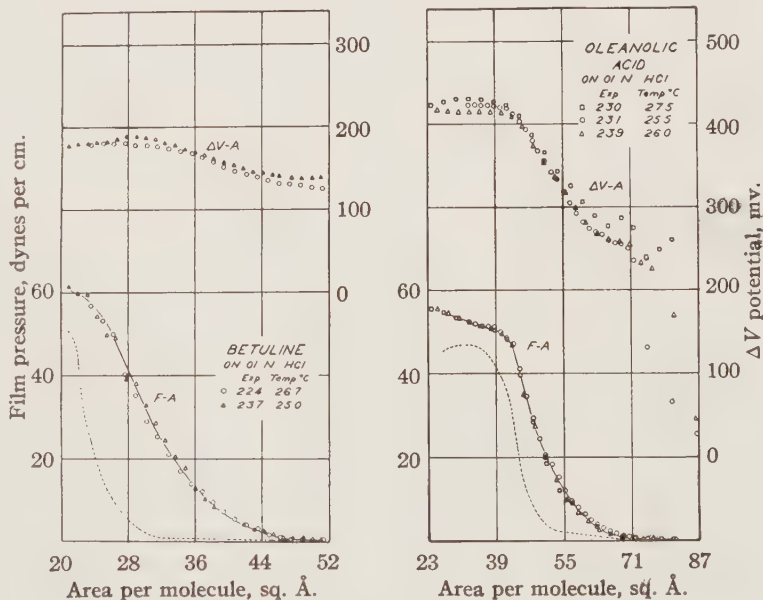


Fig. 4.

per cm. while that of betuline diacetate is only 9 dynes per cm. This illustrates the effect of changing from a strongly to a weakly polar group.

4. Molecular Rearrangement in the Films

It has been pointed out in the introduction that films of betuline exhibit a rapid rearrangement of

the molecules such that the initial pressure, developed during a compression, almost entirely disappears at lower pressures, and largely disappears at higher pressures.

resinolic acid at high but not at low pressures, and appears with films of β -amyrine and of betuline diacetate only at the higher pressures (Figs. 4-6).

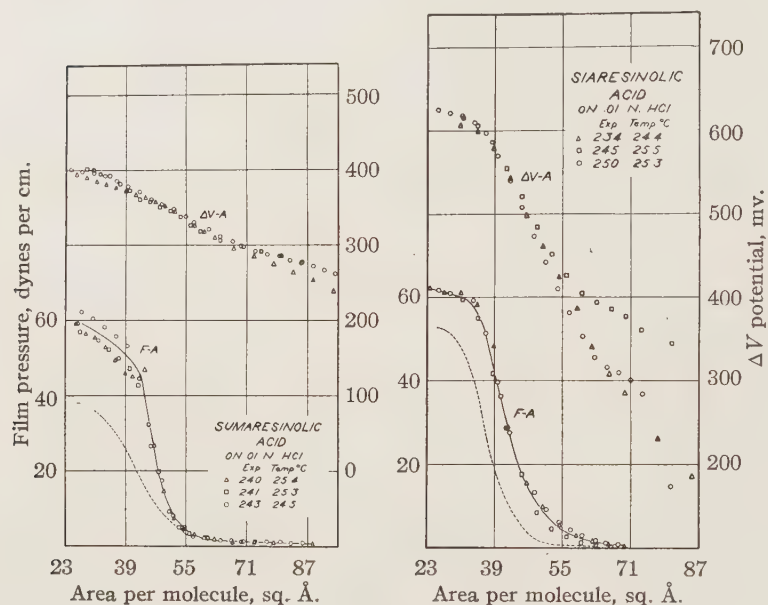


Fig. 5.

Thus the phenomenon of molecular readjustment and the resultant shrinkage of the film is very pronounced for those molecules of the five-ring type which have two highly polar groups attached to a single ring. These should be oriented toward the water. The removal of one of these groups, as in β -amyrine, or a change from hydroxyl to acetate groups, as in betuline diacetate, causes the phenomenon nearly to disappear. However, with β -amyrine on 0.02 molar hydrochloric acid Askew⁴ found a marked contraction of the film up to an initial pressure of 15 dynes per cm.

When the pressure of a film of betuline was adjusted to 16 dynes every five minutes the area decreased in an hour by 18%, but at 1.0 dyne the decrease in area was only 4.5%. If the pressure

After a compression, the film shrinks for about thirty seconds, but the total decrease in area is small. If now the area is restored to its former larger value by the extremely small expansion necessary, the pressure is greatly reduced, as from 30 dynes to 1 dyne, or from 40 dynes to 5.5 dynes. The film is now under a lower pressure, and does not under this lower pressure undergo any further contraction in five minutes. However, if the pressure is kept at the higher value (as 40 dynes) for five minutes, and the area restored to the initial value at the end of five minutes, the pressure is found to be slightly lower than if the pressure had been reduced by adjusting the area at the end of thirty seconds.

Thus the rate of contraction of the film is higher at high than at low pressures. The shrinkage of the film produces a lowering of pressure, when the area is enlarged to the initial value, which is most extreme for betuline; is also great for oleanolic and siarresinolic acids, is large for suma-

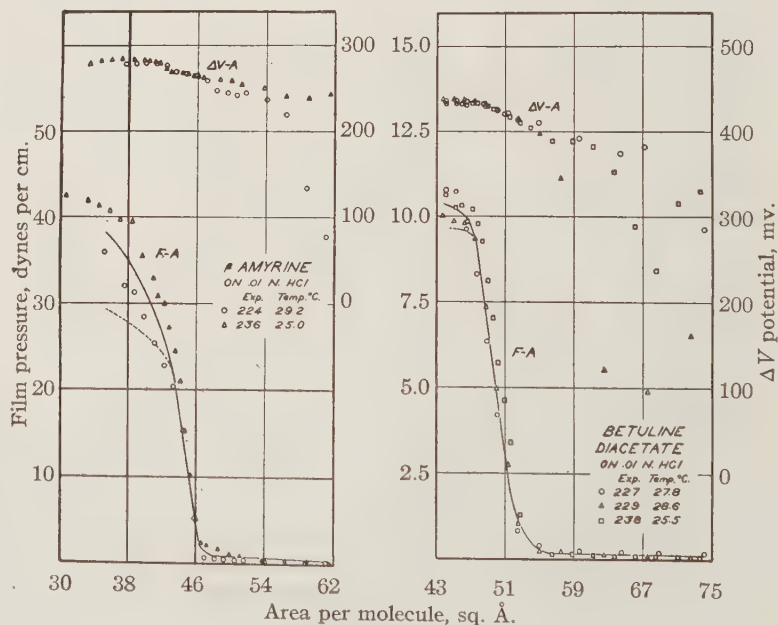


Fig. 6.

is kept constant at 16 dynes, the decrease in area occurs more rapidly.

(4) Askew, *Biochem. J.*, **29**, 472 (1935).

5. Molecular Dimensions and Orientation

Models of the five-ring compounds give a value of about 15 Å. as the length of the molecule, and indicate that the molecular area in a tightly packed film, without water present, should be of the order of 50 sq. Å. The values found at 8 dynes per cm. pressure are of this general order (Table I), with the exception of those for betuline, which seems to give a thickness of film which is anomalous, especially at the highest pressure (48.8 dynes/cm.). This indicates either that the film of this particular substance is not truly monomolecular, or that a part of the betuline has dissolved.

For the three-ring compound the model gives a molecular length of 10 Å., while the apparent film thicknesses are 9.7, 10.2 and 10.7; at zero (extrapolated), 8, and 14.7 dynes/cm., respectively.

These compounds are apparently oriented with the XY ring toward the water, and the presence of a carboxyl group at Z seems to increase the cohesion in the film.

6. Surface Potential Relations

The surface potential (ΔV) of a film composed of molecules of an organic substance is the difference between the contact potential of the aqueous surface and that of the surface when covered by the film. This is defined as positive when of the usual sign.

The data for the contact potentials of the six five-ring compounds are represented by the points of Figs. 4-6. As usual, the spread of the points at low pressures is due to non-homogeneity of the film: that is, islands of condensed film and the adjacent gaseous film are represented. In this region the highest values give the surface potential for the islands.

The shrinkage of the film produces very little effect upon the surface potential, so the data refer to either state.

The mean values for the surface potentials of the condensed films are given in Fig. 7. The surface potentials increase as the concentration in the film increases, that is, as the molecular area decreases, and most rapidly in the case of siarresinolic acid, though almost as rapidly for oleanolic acid.

The values of ΔV per molecule are represented by the values of m , where

$$m = \Delta V/n$$

in Fig. 8. Here n is the number of molecules in one sq. cm. of film. The values of $\mu = m/4\pi$ are also given in order to simplify a comparison with the results expressed by English workers. They assume that μ is the dipole moment of the molecules in the film, even although its values are commonly only one-tenth as large as the true dipole moments. It is recommended that the use of μ be discontinued, since it is the standard symbol for the dipole moment. The equation which has been used for the calculation of μ , is

$$\mu = \Delta V/4\pi n$$

This equation represents a parallel plate condenser with metallic plates, but with the dielectric constant (K) omitted. Even for this simple case the correct equation is $\Delta V = 4\pi\sigma d/K$ which they would write $\mu = \Delta VK/4\pi n$.

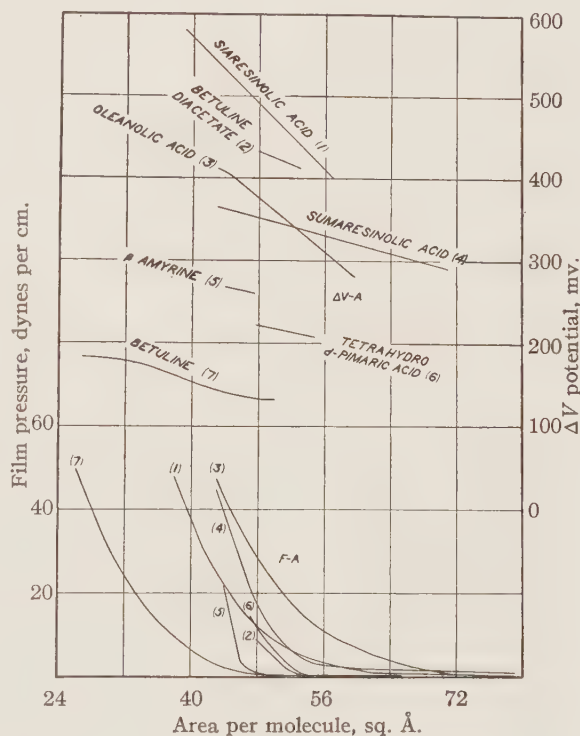


Fig. 7.

If an equation for a condenser could be applied to the case of a film, which is somewhat improbable, the value of μ would depend upon at least three dielectric constants, and the correct constant would not be 4π . It is preferable to use the value of m , which does not assume that the relation to the molecular dipole moments is known.

However, as a preliminary assumption it may be considered that the dipole moments of the molecules of the film contribute to the surface po-

tential, although other factors are involved. It is apparent that the surface potential divided by the number of molecules (m) usually decreases slightly as the number of molecules per unit area increases. That is, though the surface potential (ΔV) increases with the concentration in the film, usually the contribution of each molecule to

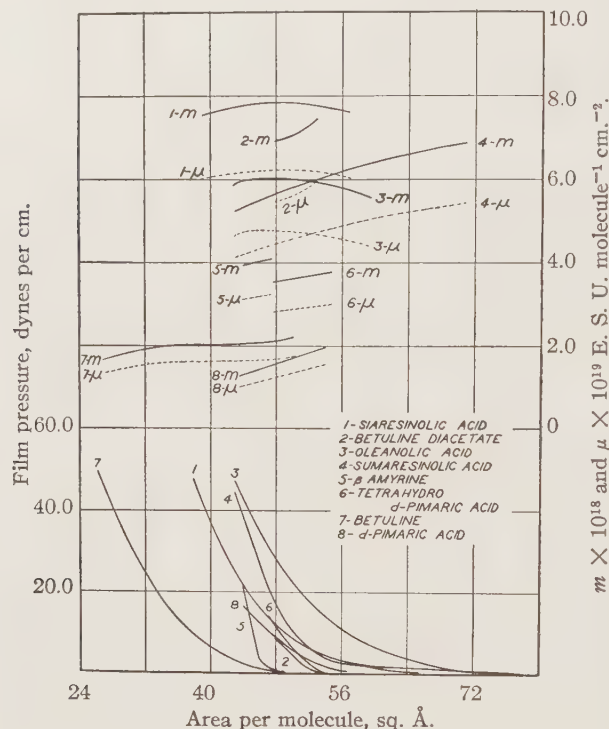


Fig. 8.

ΔV decreases with the concentration. With siarresinolic and oleanolic acids the variations are more complicated.

These relations are presented in a slightly different way in Table II, which gives the percentage increase in surface density and the corresponding percentage increase of surface potential for a specified range of surface density for the condensed film.

In general, the increase of surface density is more than sufficient to account for the increase of surface potential, but with oleanolic and siarresinolic acid the percentage increase of density is less than that of the potential.

Oleanolic acid is β -amyryne in which a hydrogen atom at Z is replaced by a carboxyl group. While with both compounds the surface potential for the condensed film is about 250 mv., the values for oleanolic acid rise to 415 mv. at 39 Å., while at the same molecular area for amyryne the surface

potential is only 280 mv. Thus, when the molecules are closely packed the carboxyl group at Z increases the surface potential by 135 mv. or by about 50%.

The substitution of a hydroxyl group in one of the lower methyl groups (Y) of oleanolic acid to give siarresinolic acid increases the surface potential at low areas from 415 to 625 mv. However, a substitution of a hydroxyl group in the same position in β -amyryne to give betuline lowers the potential by 100 mv. Thus, exactly the same substitution at Y increases the potential by 200 mv. if the carboxyl group is present at Z, and lowers it by 100 mv. if it is not present.

Sumaresinolic acid, which is a stereoisomer of siarresinolic acid, shows widely different surface potential effects. Its potential range, 290 to 400 mv., is considerably lower than that of its isomer (400 to 625 mv.), and is fairly close to that of oleanolic acid, 280 to 430 mv. There is obviously a compensation of the polar groups in the sumaresinolic acid molecule, practically amounting to the complete neutralization of the hydroxyl (Y) group. The striking feature of its potential curve, however, is that the percentage increase of the potential is only 6.67% as compared with its surface density increase of 16.8%. The compensating effect of the dipoles evidently increases rapidly on compression.

The most pronounced compensating effect of the type discussed for sumaresinolic acid was observed for *d*-pimaric acid, by Harkins, Ries and Carman.¹ As shown in Table II, the surface density increases 16.8% while the surface poten-

TABLE II
THE VARIATION OF SURFACE POTENTIAL WITH SURFACE DENSITY

Compound	Surface potential range, total	Increase of surface density, %	Increase of surface potential, %
β -Amyryne	260-285	16.8	7.44
Betuline	130-190	16.8	14.7
Betuline diacetate	410-440	16.8	8.00
Oleanolic acid	280-430	16.8	21.3
Sumaresinolic acid	290-400	16.8	6.67
Siarresinolic acid	400-625	16.8	19.5
Tetrahydro- <i>d</i> -pimaric acid	205-225	16.8	8.8
<i>d</i> -Pimaric acid	110-80	16.8	-14.1

The percentage changes are calculated from the straight portions of the $\Delta V-A$ curves, not over the total range, thus the change of surface density of 16.8% corresponds to a decrease of area from 56 to 48 sq. Å. for each compound, except for betuline (40 to 34.3) and β -amyryne (48 to 41.1), since for these two compounds the $\Delta V-A$ curves were not linear in the region between 56 and 48 sq. Å.

tial decreases 14.1% though the saturated compound, tetrahydro-*d*-pimaric acid (one polar group), exhibits normal potential relations.

As mentioned above the magnitude of the potentials of β -amyrine and betuline indicates an electrically oppositional alignment of the two hydroxyl groups in the latter molecule. It is not uncommon for a second polar group to cause a lowering of the surface potential. Similar results were found by us for *d*-pimaric acid as mentioned above and by others for certain sterols.⁵ However, too much weight should not be placed on this relationship in the particular case of betuline, since both its *F*-*A* and *V*-*A* curves are somewhat anomalous.

The high potential, 410–440 mv., of the comparatively weak film of betuline diacetate is of interest. The addition of the two acetate groups to the betuline molecule has apparently produced marked changes in the film.

The surface potentials of the condensed films vary over a large range, from 130 mv. for betuline to 630 mv. as the maximum for siaresinolic acid.

Summary

The solid monomolecular films of four of the six five-ring compounds considered in this paper have been found to give a behavior not previously exhibited, at least not in anything like this high degree. That is, if kept at constant area the pressure almost entirely disappears due to a shrinkage of the film. The behavior is more nearly analogous to that of a wax than to a crystalline solid. Thus for these films the initial pressure seems to be of much more significance than

(5) Adam, Askew and Danielli, *Biochem. J.*, **29**, 1786 (1935).

the final pressure. The initial pressures of all of the films and the surface potentials, are exhibited in Fig. 7, while the final pressures and the potentials are given in Fig. 9.

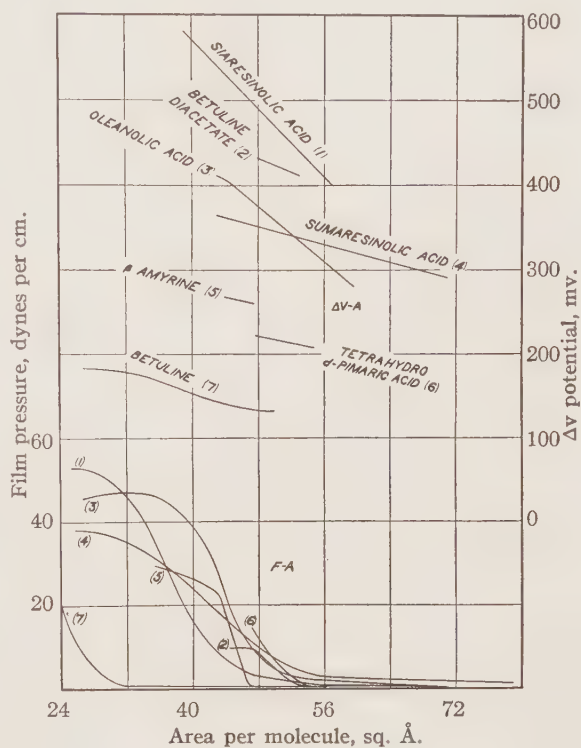


Fig. 9.

At film pressures of eight dynes per cm. the apparent thickness of the film varies from 14 to 17 Å. for the various compounds, which is about the thickness to be expected if molecules with five rings stand on end.

